Solid Prop Abstracts
Mar 1966

ON THE MICROSTRUCTURE OF COMPOSITE PROPELLANTS

Paul J. Blatz
California Institute of Technology
Pasadena, California

ON THE MICROSTRUCTURE OF COMPOSITE PROPELLANTS

Paul J. Blatz
Associate Professor of Materials Science
California Institute of Technology
Pasadena, California

I. Introduction

The term composite propellant as commonly used in the solid rocket industry refers to a heterogeneous mixture of several phases of solid particles entrained in a rubberlike binder. The two principal solid phases are aluminum fuel and ammonium perchlorate oxidizer; together with a small amount of additives which control adhesive and ballistic properties, they constitute the filler. Either a branched polyurethane or crosslinked polybutadiene network serves as a typical binder.* Performance calculations based on the assumption that the enthalpy of the composite balances the enthalpy of the combustion products at their flame temperature lead to the demand for a composite filled with slightly more than 88 wt. % of solid phases, about 25% of which is aluminum**. At this point a little arithmetic is in order.

The density of aluminum is very nearly 3, ammonium perchlorate 2, and the hydrocarbon binder 1. On this basis the volume fraction of solids is given by:

$$\nu_{sol} = \frac{\frac{\omega_{Al}}{3} + \frac{\omega_{AP}}{2}}{\frac{\omega_{Al}}{3} + \frac{\omega_{AP}}{2} + (1 - \omega_{AP} - \omega_{Al})} \qquad (1)$$

---

* Other binders are not considered in this discussion.

** These numbers are not meant to reflect the actual composition of any currently used composite, but are chosen for demonstration purposes.

Replacing the weight-fraction of ammonium perchlorate, ω_{AP}, by its equivalent

$$\omega_{AP} = \omega_{sol} - \omega_{AP} \tag{2}$$

leads with simplification to the result:

$$\nu_{sol} = \frac{3\omega_{sol} - \omega_{Al}}{6 - 3\omega_{sol} - \omega_{Al}} \tag{3}$$

Figure 1 shows that the volume fraction of solids is relatively insensitive to the weight fraction of aluminum within the range of 80 wt. %, but is quite sensitive to the total weight fraction of solids.

At a desirable level of 88 wt. % solids and 25 wt. % aluminum, the volume fraction of solids has crept up to 76.85%. At this point geometry enters the picture and points out that a unimodal distribution of close-packed spheres reach the tactile point at

$$\nu_{sol} = \frac{\pi}{3\sqrt{2}} \doteq .74 \tag{4}$$

Barring further considerations for the moment, if one endeavors to bound the volume fraction of solids by this limit, it is easily seen that this can be achieved by raising the weight fraction of aluminum to 59.2% .

As a matter of fact, it is easy to determine the maximum weight fraction of solids by inverting (3) to obtain

$$\omega_{Al} = \frac{3\omega_{sol}(1+\nu_{sol}) - 6\nu_{sol}}{1-\nu_{sol}} \tag{5}$$

Because of the necessary inequality:

$$\omega_{sol} > \omega_{Al} \tag{6}$$

it follows that:

$$\omega_{sol} < \frac{3\nu_{sol}}{1 + 2\nu_{sol}} \tag{7}$$

which, for a unimodal distribution is limited by: $\omega_{sol} < .89.5$, at which point the entire solids content is aluminum. Thus, to meet engineer's demands for high solids loading, it would be necessary to use unusually high aluminum loading. At this point however performance begins to suffer. And thus, it becomes a compelling fact that high energy composite propellants based on the fuel/oxidizer system (aluminum/ammonium perchlorate) must be filled with a polymodal distribution of particle sizes.

II. Geometry of Composite Space

A. The Uniform Bimodal Distribution.

Consider now the problem of filling an empty space with 76.85 vol. % of spherical particles uniformly distributed. Let us consider first a bimodal distribution of sizes, with particles of diameters a and b, where $a < b$.

If the large particles are first introduced into this empty space, they may be arranged either in what is known as cubic close-packing or in hexagonal close-packing. In the former case, repeating portions of the structure can be identified as cubes, each of which contains one-eighth of a sphere at each of its eight vertices, and one-half of a sphere in each of its six faces. Such a structure is also known as face-centered cubic. These $(8 \times 1/8 + 6 \times 1/2)$ or 4 spheres comprise a volume of $(2\pi/3)b^3$, whereas the

cube containing these comprises a volume of $(b\sqrt{2})^3$. Thus the maximum achievable close-packed volume fraction is $\pi/3\sqrt{2}$ or 74 vol. %.

Alternatively one might consider the tetrahedron enclosed by four nearest-neighbor spheres. This tetrahedron has an edge equal to the diameter of one sphere, and has a volume equal to $\sqrt{2}\ b^3/12$, the center of which is at a distance $b\sqrt{3}/2\sqrt{2}$ from any apex. Thus it follows that, in order to entrain spheres of a smaller size in such a repeating structure, the diameter of the smaller sphere must be less than:

$$a < b\left(\sqrt{\frac{3}{2}} - 1\right) \tag{8a}$$

or

$$\frac{a}{b} < 0.225 \tag{8b}$$

Roughly speaking, the diameter of the small spheres should not be greater than one-fifth the diameter of the large spheres. Assuming that the large-sphere structure is completely filled with small spheres, it is seen that the volume fraction of filler can be increased to:

$$\nu'_{sol} = \frac{\frac{\sqrt{2}}{12}\, b^3 \frac{\pi}{3\sqrt{2}} + \frac{\pi}{6}\, a^3}{\frac{\sqrt{2}}{12}\, b^3} < \frac{\pi}{3\sqrt{2}} + \pi\sqrt{2}\left(\frac{\sqrt{3}}{\sqrt{2}} - 1\right)^3 \tag{9a}$$

or

$$\nu'_{sol} < .7405 + .0514 = .7919 \tag{9b}$$

Thus the total solids content of a bimodally packed space can be increased by 5 vol. % over that of a unimodally packed space. Using (3) it is easily found that such a volumetric loading corresponds to 89.2 wt. % solids, of which 25 wt. % is aluminum, or, just for contrast, to 98.5 wt% solids, all of which is aluminum.

We see that, in order to achieve 88 wt.% solids loading of which 25 wt.% is aluminum, it is necessary to close-pack a space once with spheres, and then to fill again approximately one-half of the remaining interstitial space with spheres that are ca. five times smaller in diameter than those of the primary structure.

The basic building block of such a structure is the tetrahedon of volume $\sqrt{2}/12$ based on an edge equal to the diameter of a large sphere. Since the unit cube has a volume of $2\sqrt{2}$ based on the same edge, it comprises 24 tetrahedra. Furthermore, since each unit cube can contain the equivalent of 4 spheres, one tetrahedron contains the equivalent of 1/6 of one sphere. Or equivalently, since there are four spheres centered at each of the four apices of the tetrahedron, the volume of intersection is exactly 1/24 of the volume of a sphere.

As shown in eqn (9b), the available interstitial space for a small sphere located inside a unit tetrahedron is $[.0514\ (\sqrt{2}/12)\ b^3]$. In order to accommodate 76.85 vol.% loading, this interstice may be filled with a sphere of volume:

$$\frac{\pi}{6}\ a^3 = (.7685 - .7405)\frac{\sqrt{2}}{12}\ b^3 = .0280\ \frac{\sqrt{2}}{12}\ b^3 \qquad (10)$$

or equivalently, $[.0280/.0514 = 54.5\%]$ of the total number of interstices in a bulk composite may be filled with particles of maximum interstitial diameter given by eqn. (8a). Thus a/b may conveniently vary from .185 to .225.

Intuition suggests that it should be easier to achieve the situation in which a larger number of secondary particles of diameter close to .185b are used. Assuming such a situation for a moment, it is seen that the volume available to the binder in such an interstice is given by:

$$\nu_{binder} = (1 - .7685)\frac{\sqrt{3}}{12} b^3 = .027\, b^3 \qquad (11a)$$

If the primary particles are chosen to be 30 μ in diameter, then:

$$\nu_{binder} = (9\mu)^3 = 729\mu^3 \qquad (11b)$$

The secondary particles will then have a diameter of 5.55μ , and the nearest distance between a secondary and primary particle will then have a value of ca. 1μ.

A typical scale for molecular dimensions reveals that a polymer chain of molecular weight ($M = 10^6$) has a length of 1μ. Hydrodynamic measurements and elementary statistical considerations show that such root mean square end-to-end lengths are proportional to $\sqrt{M}$. This allows one to construct the following table:

$\sqrt{R^2}$, A°	M	
10^4	10^8	- corresponds to a primary chain in unfilled rubber
10^3	10^4	- corresponds to long branch or primary chain in highly filled rubber
10^2	10^2	- corresponds to short branch

It is easy to compute, assuming a density of 1 g/cc, that a typical interstitial volume in a highly filled propellant contains only 10^7 molucules of root mean square length 10^3 A°. A fortiori, it takes only ten of these molecules to bridge the gap between nearest neighbors. Thus the problem of optimizing the distribution of solid particles in a highly filled composite is strongly connected with a scale which involves the ratio of a few million polymer chains per particle. It seems immediately obvious that the degree of adhesion between these chains and a particle is going to play a tremendous role in determining some of the physical properties of the bulk composite.

In order to coat the particles the prepolymeric binder must be compensated for its cohesive energy. Typical values of the cohesive energy density of hydrocarbon molecules range around 100 cal./cc. In a unit volume of 1 cc there are 10^{-4} moles or 10^{19} molecules of molecular weight ($M = 10^4$ / and $\sqrt{R^2} = 10^3 A^\circ$. Each of these molecules makes on the average 200 contacts with neighboring molecules, assuming one-half contact for each monomer unit in the chain, and taking the submolecular weight of a monomer unit to be 100. Thus it takes about 5×10^{-20} cal. to break a contact. Now on a surface of 10^6 $A^{\circ 2}$, there will lie about 500 such polymer chains, assuming a spacing of about $2A^\circ$ between chains. And such a surface will provide 5×10^4 contacts. Thus it should take about 25×10^{-16} cal. to generate a surface of $10^6 A^{\circ 2}$, or 25×10^{-6} cal. (10^3 erg) to generate a surface of 1 cm^2. Even though this crude calculation be off by a factor of ten, it follows that hydrocarbon surface free energies are extremely low. A realistic figure is probably closer to 100 erg/cm^2. It should not be surprising to find that cohesive failure in a binder precedes any other type of physical damage. Attention has already been called to this point by Oberth and Bruenner[1]. In addition, creep failure experiments[2] suggest that cohesive failure in rubber is a quite common occurrence.

By the same token, but for a different reason which involves charge separation, the surface free energy of ammonium perchlorate is also of the order of 100 ergs/cm^2. That of aluminum is of the order of 800 ergs/cm^2. By themselves these numbers mean nothing, for the adhesion resulting from the adjunction of two free surfaces surely depends, as Bikerman[3] suggests, on the free energy change brought about by dipole-dipole and induced dipolar interaction. An adequate theory of such effects is yet to be forthcoming. In

the absence of such a theory, it is convenient to note that measured energies of adhesion (via contact angle) suggest a value of about 100 erg/cm^2 for the spreading of binder upon ammonium perchlorate.

It is of interest to note what affect this adhesive energy may have upon the distribution of particles. Remembering that a/b may range between .185 and .225, it is to be expected that the increase in heat of wetting produced by using a larger number of smaller secondary particles will bias the situation in that direction for a given desired total solids loading. On the other hand, the entropy is maximized by filling only half the interstices. The result of this competition is exposed by noting the following relations.

The free volume of a composite composed of N tetrahedra, N_a of which are occupied by secondary particles of diameter a is given by:

$$1-.7685=.2315 = \frac{N_a\left(\frac{\sqrt{2}}{12}\,b^3 - \frac{\pi}{36}\,b^3 - \frac{\pi}{6}\,a^3\right) + \left(N-N_a\right)\left(\frac{\sqrt{2}}{12}\,b^3 - \frac{\pi}{36}\,b^3\right)}{N\,\frac{\sqrt{2}}{12}\,b^3} \tag{12a}$$

or

$$.006302 = (.185)^3 = \frac{N_a}{N}\,(a/b)^3 \tag{12b}$$

Eqn. (12b) paraphrases what has already been made clear. When $N_a = N$, $a/b = .185$; when $a/b = .225$, $N_a/N = 54.5\%$. The measure of the thermodynamic probability of a distribution of secondary particles of diameter a is given by:

$$W = \frac{N!}{N_a!\,(N-N_a)!}\,e^{E_{adh}/kT} \tag{13}$$

The energy of adhesion E_{adh} is given by:

$$E_{adh} = \left[N_a \left(\frac{\pi}{6} b^2 + \pi a^2 \right) + (N - N_a) \frac{\pi}{6} b^2 \right] \epsilon_a \qquad (14)$$

where ϵ_a is the specific energy of adhesion taken to be 100 ergs/cm^2. Using (12b) and (14), (13) can be maximized with respect to N_a, leading to the relation:

$$\frac{N_a^*}{N} = \frac{1}{1 + \exp - \left[\frac{\epsilon_a \pi b^2}{kT} \frac{(.185)^2}{3} \left(\frac{N}{N_a} \right)^{2/3} \right]} \qquad (15)$$

Because adhesion energies are so low relative to (kT), the factor multiplying $(N/N_a)^{2/3}$ is of the order of 10^{-6}, and thus $N_a^*/N = 1/2$; the random character of the distribution is unaffected by the adhesion. Since the lower limit of N_a^*/N is already slightly greater than 1/2, as required by the limitation upon the size of a secondary particle in an interstice, it follows that thermodynamics suggests that it is desirable to use the largest secondary particles possible, namely (a/b = .225).

There are however, other factors involved in determining the distribution of secondary particles. In the first place, the particles are not distributed among the tetrahedral interstices by a process of penny pitching. They are distributed by mechanical forces in an operation which involves both grinding and viscous forces. Assuming that comminutive forces are reduced by reducing the number of contacts it follows that it is desirable to use the smallest allowable value of a/b. That this is actually the case is suggested by the work of Gillis and Leeming[4], who find that blends which are optimized in a certain sense which we will define later evince more

desirable properties. By implication, Leeming and Gillis'[4] work rules out nonuniform distributions, such as would be the case if only 54.5% of the secondary holes were filled.

We can summarize the situation at this point by stating that neither enthalpic nor entropic effects determine the optimum spatial distribution of secondary particles. Accepting for the present the assumption that a uniform spatial distribution is desirable (a/b close to .185 and all secondary holes filled), it then becomes obvious to suggest that the primary structure be reduced in size while the secondary be increased to compensate for it. This has the advantage of further reducing the number of contacts.

B. The Random Distribution.

With the added degree of freedom involved with the variation of the size of the primary particles, there are now an infinite variety of combinations of diameters a and b which will still provide a total solids loading of 76.85 vol.% and also maintain uniform spatial distribution of both the primary and secondary particles. The defining relation is given by:

$$.7685 = \frac{\frac{\pi}{36} b^3 + \frac{\pi}{5} a^3}{\frac{\sqrt{2}}{12} \ell^3} = \frac{\pi}{3\sqrt{2}} \beta^3 + \pi\sqrt{2}\ \alpha^3 \qquad (16)$$

where $\beta \equiv b/\ell$ (17)

$\alpha \equiv a/\ell$ (18)

and ℓ is some arbitrarily chosen length scale, say 30μ. Eqn. (16) still shows that when $\beta = 1$, $\alpha = .185$. On the other hand, the lower limit of β is determined by the fact that a cannot exceed that particular diameter which is the diameter of the largest inscribed sphere in a tetrehedron. This can

be shown to be ($a = e / 2\sqrt{2}$), at which point $\beta = .917$.

Now what will happen in practice, of course, if one (speaking hypothetically) were to distribute uniformly in space primary spheres of diameter $\beta = .95$, say, and secondary spheres which had an α that satisfies eqn. (16), is that the spheres would agglomerate making for relatively looser and relatively denser regions. In addition, another degree of freedom can now be added to the picture. Consider two such regions, within a given mass of bulk composite, each characterized by a different value of β (each β having associated with it an α given by (16)). It is possible for the two regions to exchange particles without disturbing the general uniformity of the overall distribution. This is because the secondary particles are free to rattle around in the interstices, and this in turn arises because roughly half of the available free volume available to secondary particles is unoccupied at the loading level of .7685. By allowing indiscriminate interchange of all particles it is possible to increase tremendously the entropy of such a composite without significantly changing the number of contacts between particles.

Let us now add another degree of freedom. Suppose the edge scale, taken above to be 30μ, is also allowed to vary. Now a new problem arises. Consider two subregions, one based on a primary particle scale of 30μ which can range down to 91.7% of that (along with its associated secondary particles) and all the previously allowed mixing variations, and another subregion based on a primary particle scale of 60μ which can range down to 91.7% of that (along with its associated secondary particles and mixing). It is now impossible to interchange particles between the two regions without disturbing the spatial uniformity of packing or without seriously affecting the number of contacts. These statements can be documented mathematically and are associated with problems that arise in alloy structures. It is not

necessary however to describe the problem mathematically. The solution can be seen very easily in a qualitative sense.

The main idea is that each set of spatially uniformly distributed primary particles requires an associated set of secondary particles which are roughly five times smaller in diameter. If a polymodal distribution of sizes is provided then the following situation develops. Let us assume there are four sizes: 1, 1/5, 1/2, and 1/10. It is possible for a particle of size 1/10 to enter a tetrahedral interstice in a region populated by primary particles of size 1. But the corresponding reverse exchange in which a particle of size 1/5 enters a tetrahedral interstice in a region populated by primary particles of size 1/2 is not possible, not at least without significantly disturbing the spatial uniformity of packing. One way out for the displaced particles of size 1/5 is for them to set up their own primary structure, but in order to do so, they need secondary particles of size 1/25. By the same token, the parent particles of size 1, which are now not contributing their full share by housing particles of size 1/10 can take on a new role of secondary particles (dragging their minor satellites of size 1/10 along with them), if there were available new primaries of size 5. This situation can be handled by providing a continuous distribution of particle sizes, enough so that when a few particles of the same size get together, they can decide to be either a primary structure or a secondary structure depending on what else is available in the neighborhood. It is obvious that this cannot be the case if the distribution is highly discontinuous.

The situation can be summarized with the statement that, in dealing with volumetric loadings that exceed $\pi/3\sqrt{2}$, it is necessary to provide for small regions of bimodal character. Thus, even though the size distribution

may be quite uniform and quite broad, the basic packing character must remain bimodal.

It is a fact established by the fine work of Leeming and Gillis[4] that the desired size distribution is best achieved by a log normal population.

III. Deformation of a Composite Space

When a composite space comprised of two essentially incompressible phases (solid particles and rubber binder) is deformed, dilatation and attendant vacuole formation are necessary consequences. The fact that some composites do not seem to dilate within the application of a few percent tensile strain merely indicates that there is already present in the composite an equivalent amount of void space, say .1 or .2 %, which is taking up the initial slack. In addition it should be remembered that a composite material, to the extent that it resembles a granular material, is statistically indeterminate, so that there are many allowable configurations of the particles consistent with a given stress level.

After the initial slack is taken up, dilatation does indeed occur. Farris[5] was the first to recognize that the dilatation process per vacuole is essentially a random process. His reasoning goes as follows. He assumes that the volume of the vacuole developed around a particle is directly proportional to the average strain in the composite under uniaxial stress. Then the total dilatation is proportional to the product of the strain and the number of particles around which vacuoles have developed. Once one accepts this idea it is a simple matter to look at data and note that the fractional number of dewetted particles is a cumulative probability function of the strain. Analytically speaking, the data suggest that:

$$\frac{d\vartheta}{d\epsilon} = C\nu_d = C\left[\frac{\nu_{sol} - \nu_o}{\sqrt{\pi}} \int_{-\frac{\bar{\epsilon}}{s\sqrt{2}}}^{\frac{\epsilon - \bar{\epsilon}}{s\sqrt{2}}} e^{-u^2}\, du + \nu_o\right] \tag{19}$$

where ν_d is the volume fraction of total solids which are dewetted at any given strain level.

ν_o is the volume fraction of total solids which are dewetted in the undeformed composite.

C is a proportionality constant which Farris' data indicate is clearly unity.

s and $\bar{\epsilon}$ are respectively the mean and standard deviatoric strains obtained from a plot of $d\vartheta/d\epsilon$ vs ϵ on linear probability paper.

ϑ is, of course, the dilatation = $\Delta V/V^+$, where V^+ is the undeformed volume.

Eqn (19) may be recast in alternate form (with C = 1):

$$\frac{d\vartheta}{d\epsilon} = \nu_o + \frac{\nu_{sol} - \nu_o}{2\sqrt{\pi}}\left[\int_0^{(\frac{\bar{\epsilon}}{s\sqrt{2}})^2} \frac{e^{-v}\, dv}{\sqrt{v}} + \int_0^{(\frac{\epsilon - \bar{\epsilon}}{s\sqrt{2}})^2} \frac{e^{-v}\, dv}{\sqrt{v}}\right], \quad \epsilon > \bar{\epsilon} \tag{20a}$$

$$\frac{d\vartheta}{d\epsilon} = \nu_o + \frac{\nu_{sol} - \nu_o}{2\sqrt{\pi}}\left[\int_{(\frac{\bar{\epsilon} - \epsilon}{s\sqrt{2}})^2}^{(\frac{\bar{\epsilon}}{s\sqrt{2}})^2} \frac{e^{-v}\, dv}{\sqrt{v}}\right], \quad \epsilon < \bar{\epsilon} \tag{20b}$$

The integrands on the right hand sides of (20) are incomplete gamma functions. For small strains, (20b) can be expanded to yield:

$$\frac{d\vartheta}{d\varepsilon} = \nu_o + \frac{(\nu_{sol} - \nu_o)\ \varepsilon}{\sqrt{\pi}\qquad s\sqrt{2}} \tag{21}$$

which may be integrated to:

$$\vartheta = \nu_o \varepsilon + \frac{\nu_{sol} - \nu_o}{s\sqrt{2\pi}}\ \frac{\varepsilon^2}{2} \tag{22}$$

Now Farris[5] has also recognized that the slope of the uniaxial stress-strain curve decreases with strain at a rate which is proportional to the volume fraction of dewetted solids, or in analytical terms:

$$\frac{d\sigma}{d\varepsilon} = E_1 - E_2\ \nu_d = E_1 - E_2\ \frac{d\vartheta}{d\varepsilon} \tag{23}$$

This may be integrated to yield:

$$\sigma = E_1\ \varepsilon - E_2\ \vartheta \tag{24}$$

Under the approximation (22), (24) becomes

$$\sigma \simeq (E_1 - E_2\ \nu_o)\ \varepsilon + \text{terms of higher order} \cdots \tag{25}$$

Thus the usually accepted definition of Young's modulus from infinitesimal theory may be equated to $(E_1 - E_2\ \nu_o)$. At this point the writer takes the liberty of pointing out that E_2 should be related to the adhesive stress per particle and should be calculable from the sort of relations that were introduced in Section II. Similarly E_1 should be calculable from the modulus of the unfilled binder and the total volume fraction of solids.

The resulting situation may be summarized by stating that stress-strain behavior in composite materials may be quite well understood in terms of a quasi-linear theory constructed from ordinary linear theory in which the parameters (Young's modulus and Poisson's ratio) are replaced by new parameters which depend upon the dilatation, which in turn has been shown to be a random function of the particle dewetting process.

In closing this discussion, it should be noted that Farris[5] has also indicated that uniaxial fracture seems to occur at ca. 3 standard deviations from the mean strain. It remains to document this criterion with suitable data in other stress fields. This, of course, implies measurement of dilatation in the biaxial stress field.

REFERENCES

1. Oberth and Bruenner: ICRPG Bull., 4th Meeting Bulletin, Vol. II, p. 45.

2. Kawabata, S.; Blatz, P. J.: "Creep Failure Studies on SBR Vulcanizates, I." MATSCIT PS 65-6, California Institute of Technology, September 1965. (Presented at the meeting of the Division of Polymer Chemistry of the American Chemical Society, November 1965). Rubber Chemistry and Technology, (in press).

3. Bikerman, Trans. Soc. Rheol. 3, 5 (1949).

4. Gillis and Leeming: ICRPG Bull., 4th Meeting Bulletin, Vol. I, p. 1.

5. Farris, ICRPG Bull., 4th Meeting Bulletin, Vol. I, p. 105.

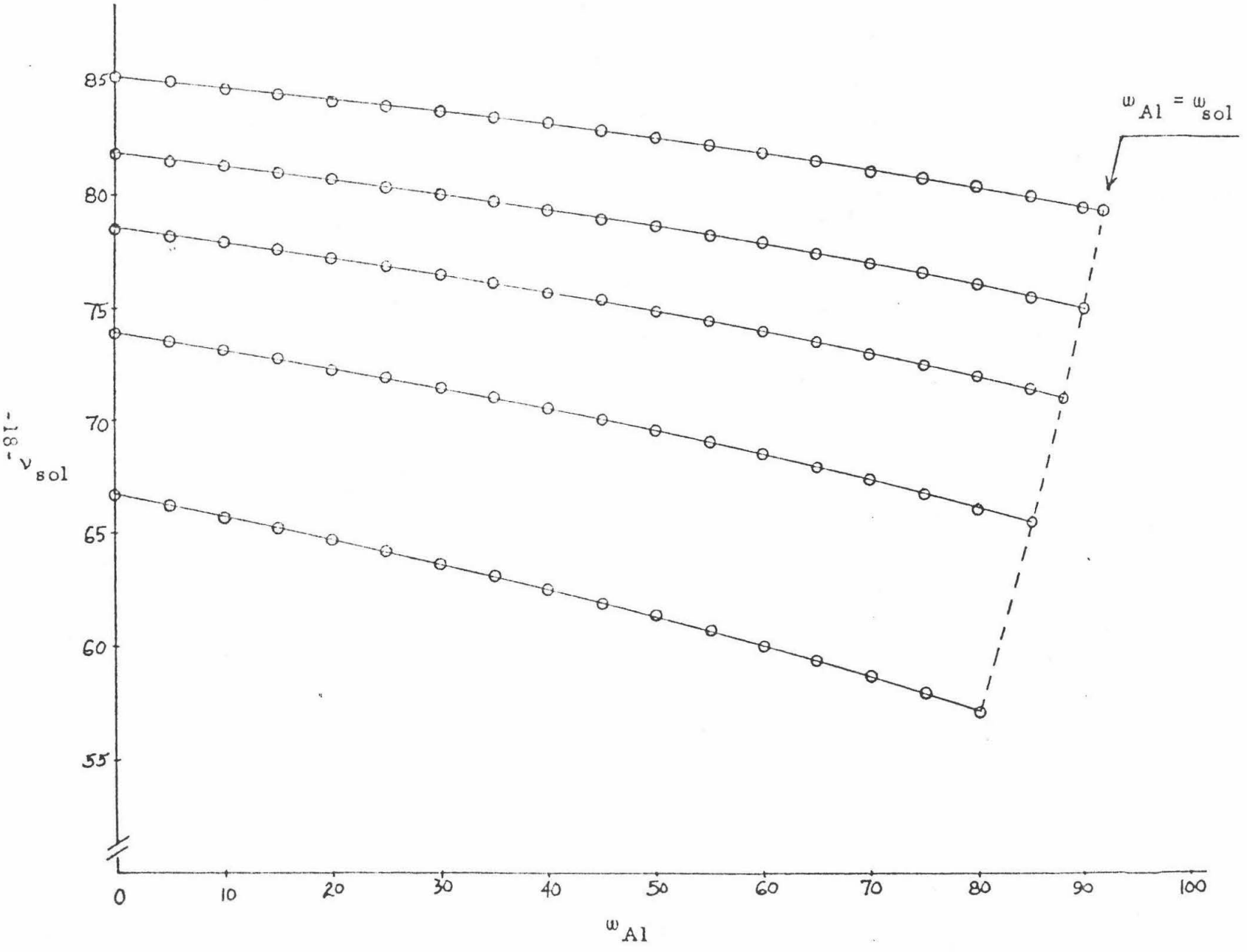

Figure 1. Correlation Between Volumetric and Weight % Solids Loading for Al/AP/HC Composite Solid Propellants.